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STUDIES IN THE FURANE SERIES

BY

EDWARD TILLSON HOWELL

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DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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STUDIES IN THE FURANE SERIES

I. INTRODUCTION AND HISTORICAL.

Heterocyclic compounds such as furfurane, thiophene and pyrrol, undergo many of the reactions peculiar to benzene. Compounds of the furane series, especially, possess to a very marked degree the characteristics of the corresponding aromatic compounds.

The original problem was to see if the analogy between the furane and benzene series reached to the extent that the furyl amine, corresponding to aniline, could be prepared from pyromucic acid amide by the Hofmann hypochlorite reaction. Pyromucic acid was not purchasable, so in the course of making it, the investigation was extended to include a method for the preparation of pyromucic acid on a semi-commercial scale.

As early as 1832 (1) Doebereiner had prepared furfural by distilling sugar with pyrolusite and dilute sulfuric acid. It has since been prepared from certain pentoses, bran, wood, or corn cobs, digested with dilute hydochloric acid and distilled.

Until 1901, the best method for preparing pyromucic acid was that given by Volhard in 1891 (2). He oxidized furfural with potassium permanganate in the presence of a large excess of potassium hydroxide. In 1901, the English chemists, Frankland and Aston, (3) published a new method. They used calcium hydroxide instead of potassium hydroxide, and much less water. The temperature in both these methods was kept well under 20 degrees. Frankland's method gave a much cleaner product, due to the fact that in the Volhard method, the strong KOH solution tends to form sticky, tarry polymerization products

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[illegible]

[illegible]

[illegible]

[illegible]

from furfural. For the sake of comparison, if the amount of furfural used in each of these methods is made 1 mole, and the other materials changed in proportion, the result is as follows:

	Volhard		Frankland-Aston	
Furfural	1	mol	1	mol
Water	4000	cc	500	cc
Permanganate	.66	mol	.66	mol
Water	4000	cc	2000	cc
Calcium hydroxide. . . .			2.63	mol
Potassium hydroxide. . .	.464	mol		
Per cent. yield	79	%	62.5	%

From this it is seen that although Frankland-Aston got a smaller per cent. yield, their method is much better, because it gives a much cleaner product, and cuts down enormously on the amount of water used, which is an item of very great importance if the acid is to be manufactured on a commercial scale.

Pyromucic ethyl ester was made in 1838 by Curtius-Leimbach, (4), by saturating an alcoholic solution of pyromucic acid in the cold with HCl gas. The method gives 50-60% yields. The ester when heated with aqueous ammonia in a sealed tube gives the amide (5). This was done by Schwanert in 1860. The amide can also be prepared from the acid chloride, a method for which was published in 1901 by Frankland (6). He treated a chloroform solution of pyromucic acid with phosphorous pentachloride in a special apparatus. The amide is made from the acid chloride by dropping it into aqueous ammonia(7).

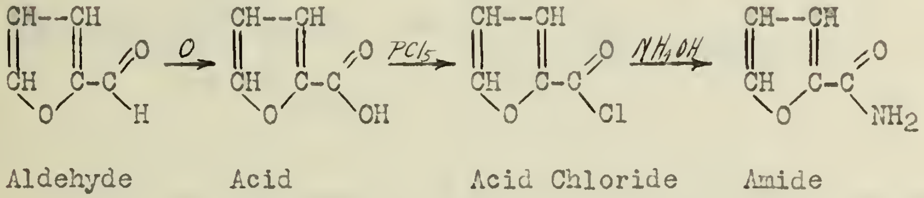
The only mention of the Hofmann reaction on pyromucic acid amide that could be found in the literature was an article by Freundler in 1897 (8), who said in part, that when puromucic acid amide was

heated with alkali hypobromite, nitrogen and carbon dioxide were given off, and the solution became strongly alkaline with ammonia. No mention was made, however, of what else was formed, nor were the conditions given under which the reaction was carried out.

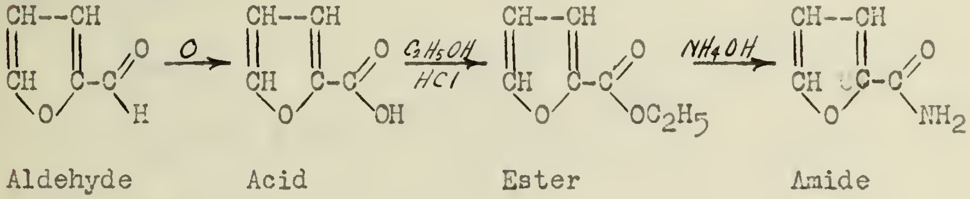
II. THEORETICAL.

Since the amide was not obtainable, it had to be made, starting with furfural, the aldehyde. Two methods were possible, as outlined in the following schemes:

A)


O
PCl5
NH4OH
Aldehyde
Acid
Acid Chloride
Amide

B)


O
C2H5OH
HCl
NH4OH
Aldehyde
Acid
Ester
Amide

Due to the fact that the acid chloride was extremely obnoxious, and decomposed easily, the second, or ester method, was used almost entirely in making up a supply of the amide, which was to be treated next by the Hofmann reaction.

According to Weyl, an amide when treated with bromine and NaOH, theoretically goes through the following reactions:

(In this case, the "R" group is the furane ring,)

[illegible]

[illegible]

[illegible]

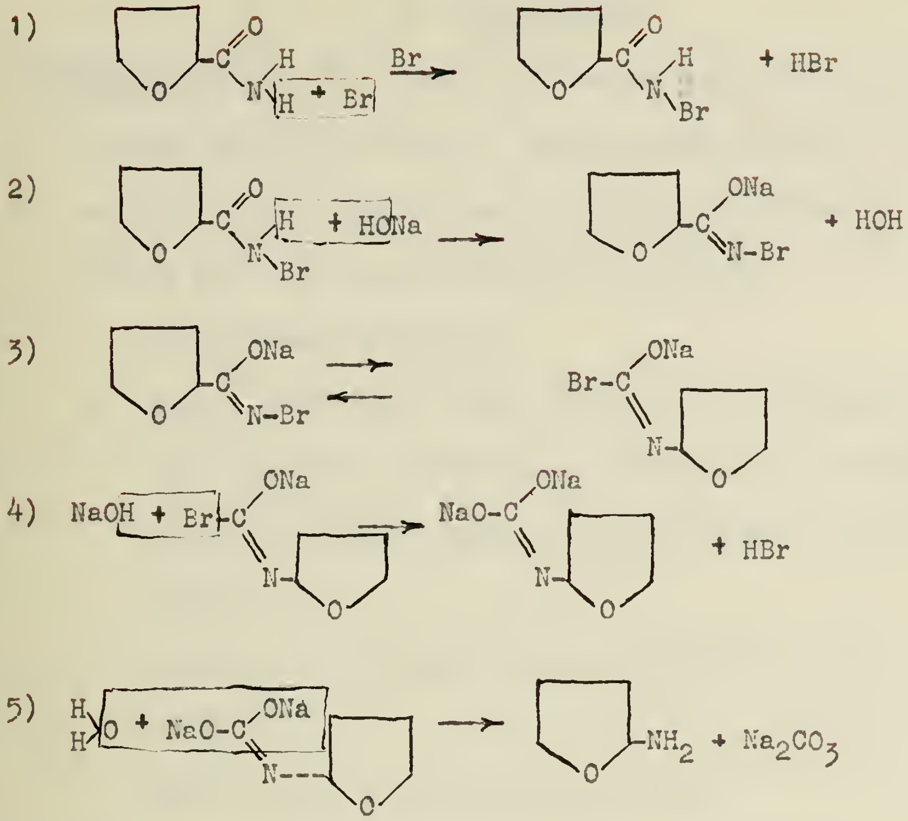
$$[illegible]$$

[illegible]

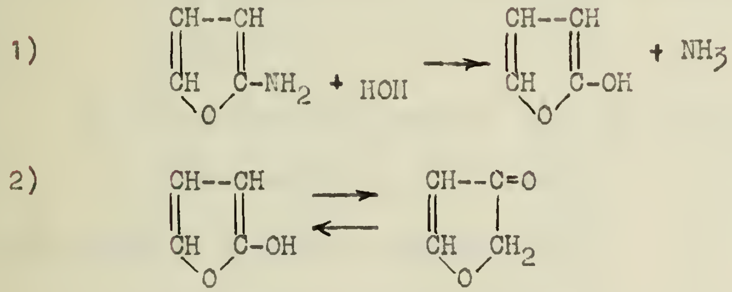
$$[illegible]$$

[illegible]

[illegible]


1)
Br
+ HBr
2)
+ HONa
+ HOH
3)
ONa
N-Br
Br-C
4)
NaOH + Br
NaO-C
+ HBr
5)
NH$_2$
+ Na$_2$CO$_3$

It is then possible that the amine may hydrolyze as follows, giving a phenol:


1)
CH--CH
CH C-NH$_2$ + HOH
CH C-OH
+ NH$_3$
2)
CH--C=O
CH CH$_2$

III. EXPERIMENTAL.

1) PYROMUCIC ACID. This was in all cases prepared from furfural by various oxidation methods. The furfural was made in the Laboratory of Organic Manufacture by digesting ground corn cobs in dilute HCl, and then distilling the mixture.

The methods tried were:

a) Method of Volhard, which consists of oxidizing furfural in the cold with the theoretical amount of permanganate, in the presence of large excess of NaOH, keeping the mixture well stirred.

b) Oxidation in the cold with potassium dichromate in the presence of acid.

c) Oxidation with 35% hydrogen peroxide.

d) Volhard method with the addition of ether.

e) Method of Frankland-Aston. An oxidation in the cold, using permanganate, and large excess of calcium hydroxide as the alkali.

f) Frankland-Aston method with the addition of ether.

Since methods a, d, e, and f, only, gave desirable results, the others will not be described here.

The general method followed in the preparation of pyromucic acid was as follows: The furfural was first mixed with the alkali and water in a round bottom flask. The theoretical amount of permanganate in solution was then added in small portions with cooling and agitation. In the first few trials, the flask, which was cooled by a stream of water, was merely agitated by hand. In all the later runs, however, the mixtures were cooled in ice-salt baths, and more efficient-

ly agitated by means of mechanical stirrers. After completion of the oxidation, the mixture was heated on the steam bath for a few hours to coagulate the precipitate of MnO_2, which was filtered off, the solution of the metallic salt of pyromucic acid evaporated down, acidified with HCl, and the pyromucic acid crystallized out, or else extracted with ether, to get the crude acid.

In the Volhard method, KOH or NaOH is the alkali, while in the Frankland-Aston method, calcium hydroxide is used. The latter gave a much cleaner product and better yields, as may be seen from the following table. Since different quantities were used in different runs, in order to get a better comparison of results in the table, all the quantities were changed to the basis of 1 mole of furfural, while the actual amount of furfural used has been given in the third column.

No	Method	Actual amount furfural	Alkali, Basis 1 mol furf.	Ether	Total water, basis 1 mol furf.	% yield crude acid	Remarks
1	Volh.	0.2 mol	260g NaOH		8000 cc	44%	Hand stirring
2	"	0.2 "	260		5500	24%	" "
3	"	0.2 "	260		5000	31%	" "
4	"	0.2 "	260		8000	64%	Slower add. of $KMnO_4$
5	"	0.625 "	260		8000	60%	Mech.stirring, ice
6	"	0.75 "	275		6660	51%	" " "
7	"	1.0 "	250		4500	50%	" " "
8	"+ether	1.0 "	250	20cc	2500	45%	Purer product
9	" "	2.0 "	125	25cc	1700	75%	" "
10	Frankl.	2.085 "	144 $CaOH_2$		2400	43%	No ether used
11	"+ether	1.04 "	144 "	20cc	1825	56%	Ether used
12	" "	1.565 "	144	20cc	2050	52%	Purer product
13	" "	2.085 "	144	25cc	3120	60%	
14	" "	2.085 "	144	25cc	3120	65%	Very pure product

In looking over the different methods, perhaps the most striking thing in the first seven runs, is the influence which the

amount of water had on the yields. The explanation of this seemed to be, that the larger the mass of water in proportion to furfural, the greater was the chance for it to emulsify, and hence to give better yields. Consequently, it was thought that if something could be added to increase the emulsification, or even solution of furfural, the amount of water could be decreased. The original Volhard method would hardly be practical commercially, since it requires such large volumes of water in proportion to the amount of acid obtained. To increase emulsification, a quantity of ether was added, which would just dissolve in the amount of water used. The results are quite positive. Taking the average of volumes of water used, and per cent yields, before and after using ether, the results based on one mole of furfural are:

	Method	Total water used	Per Cent Yield
A)	Volhard (without ether)	6500 cc	46%
	Volhard (with ether)	2100 cc	60%
B)	Frankland (without ether)	2400cc	43%
	Frankland (with ether)	2500cc	58%

The choice lies between the Volhard method with ether, and the Frankland method with ether. The former seems to have some slight advantage, on account of using less water, and at the same time giving a little better yield. However, this advantage is more than overcome by the cleaner product given by the lime method. By using ether with the lime method, the amount of water was cut down to less than one-third of that used in Volhards original method.

Taking all this into consideration, if a method were desired for making pyromucic acid on a large scale, the lime-ether method is the one to be recommended.

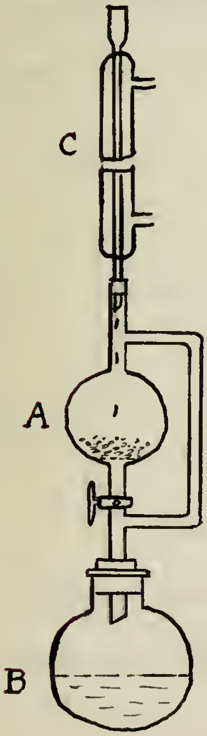
2) PYROMUCIC ETHYL ESTER.

The method of Curtius-Leimbach was used. (4). This consists of esterifying pyromucic acid in the cold with ethyl alcohol, using HCl as a catalyzer by saturating the alcoholic solution with dry HCl gas. The greater part of the excess alcohol is distilled off. The remainder with ester in solution, is poured into cold water, and extracted with ether. The ester can be purified by distillation under diminished pressure.

RESULTS.

No.	Pyromucic Acid	Alcohol	Per Cent Yield
1	75 g	375 cc	51%
2	75 g	375 cc	46%
3	75 g	375 cc	42%
4	85 g	400 cc	58%
5	100 g	500 cc	42%

3) PYROMUCYL CHLORIDE.



The method described by Frankland (6) was followed. Dry pyromucic acid is placed in bulb "A", while a solution of phosphorous pentachloride is boiled in flask "B". The chloroform vapors from the solution in "B", pass by way of the side tube up into the condenser "C", from whence chloroform drops back through the pyromucic acid, carrying some of the latter drop by drop into flask "B". Here the pyromucic acid reacts with PCl_5, and is converted into the acid chloride. The method worked fairly

well, but no data was obtained on yields due to the fact that the product decomposes somewhat, and is extremely obnoxious to handle. the method was finally abandoned in favor of the ester method.

4) PYROMUCIC ACID AMIDE.

After a few trials, it was found that dry ammonia was without effect on pyromucic ester. In 1860 Schwanert (5) prepared the amide by heating the ester in a sealed tube with aqueous ammonia. This suggested the use of an autoclave or bomb. A steel bomb made of a section of 3 inch gas pipe, fitted with a pet cock, lined with lead, and having a capacity of approximately one liter, was used for this purpose. The procedure was as follows: Dry ester was placed in the bomb, covered with excess ammonia water, and heated in a water bath at about 90° under high pressure for 24 to 36 hours. On cooling and removing the cap, a mass of white warty crystals separated out, which were purified by crystalization from water. A melting point taken on each run agreed closely with that of pure amide. (141-142°)

RESULTS.

No.	Ester	NH_4OH	Per Cent Yield	Remarks
1	10 g	100 cc	19%	Pressure flask used
2	10 g	100 cc	14%	" " "
3	40 g	400 cc	44%	H P bomb used
4	106 g	600 cc	46%	" " "

Both bomb and pressure flask leaked to certain extent, although the former leaked less than the latter, as is shown by the increased yields. With an air tight bomb the yields should be 90%.

5) THE HOFMANN REACTION.

a) 1st Run

Amounts Used:

Pyromucic Amide	15 grams
Bleaching Powder	50
Sodium Carbonate	50

The amount of bleaching powder and sodium carbonate used was enough to give approximately 30 grams NaOCl in solution. There was no apparent reaction when the dry amide was treated with the hypochlorite solution in the cold. However, on heating the mixture on the steam bath, it became very dark brown, and the odor of ammonia was distinctly perceptible. The alkaline mixture was refluxed for about an hour, ammonia being evolved all the while. Two distillations were run; one on the alkaline mixture, and the other after it had been acidified. After slowly evapoating these distillates down and extracting with ether, there were no residues after evaporation of the ether. The acid residue in the distilling flask, however , on extraction with ether, yielded a brown powder, which after recrystallization from water, was identified by mixed melting points as pyromucic acid. The first run, then, showed that part of the amide is hydrolyzed back to the original acid.

b) 2nd Run

Amide	18 grams
Bromine	30
NaOH	13

The amide, which was dissolved in the NaOH solution, was treated with bromine added in small portions with stirring. Vigorous reaction

requiring cooling took place, but there was no odor of ammonia. The alkaline mixture was then distilled over a Bunsen burner, and the distillate extracted with ether. A slight oily residue, smelling stongly of an amine (similar to aniline) remained on evaporating off the ether. The original mixture also smelled very strongly of amine. The substance obtained was of too small a mass to work with. The residue in the distilling flask, which was acidified and extracted with ether, again yielded a small amount of pyromucic acid.

c) 3rd Run.

Amide	7 grams
Bromine	15
NaOH	15

In this run, the amide was first dissolved in bromine water in the cold, and the NaOH added in small quantities. Vigorous reaction requiring cooling ensued, accompanied by evolution of a gas having no odor, which was probably CO_2 or nitrogen according to Freundler (8). No ammonia odor was perceptible. No products were obtained by distilling the mixture in the presence of acid or alkali; but the alkaline residue in the distilling flask, smelling strongly of an amine, yielded a trace of oily substance on extraction with ether. The acid residue again contained small amounts of pyromucic acid.

The strong odor partly resembling that of aniline, but more like an aliphatic amine, was taken as an indication that the heterocyclic amine was formed in small quantities. More work is to be done on this subject later.

IV. SUMMARY.

1) PYROMUCIC ACID.

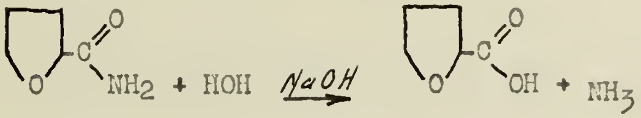
One-half pound of pyromucic acid can easily be made in a 7 liter volume, with yields varying from 50 to 80 per cent, depending upon the care in manipulation. Formerly a volume of 15 liters would have been required for preparing the same amount of pyromucic acid by the Volhard method giving a 45 per cent yield.

2) PYROMUCIC ETHYL ESTER AND PYROMUCIC ACID AMIDE.

Methods for the preparation of the ester and amide have not been so carefully worked out as for the acid, but yields of 50 to 60 per cent can be obtained with no difficulty at all on the ester, while the amide can be prepared with 40 to 50 per cent yields. There is no doubt but what these can be greatly increased.

3) THE HOFMANN REACTION.

In each case where a Hofmann reaction was tried, using either hypochlorite or hypobromite, it was found that one of the products was pyromucic acid, which was formed from the amide by hydrolysis, probably according to the following reaction.



On treating the amide in the cold with hypochlorite and then heating, ammonia is given off. On treating the amide in the cold with hypobromite a gas with no odor was given off. This was probably CO_2 or N_2.

When the amide is treated with hypobromite, the reaction

mixture, on standing, possesses an odor similar to aniline, yet more like an aliphatic amine. This was taken as an indication that the heterocyclic amine was formed to some extent, although in quantities too small to work with. The same work is to be carried further in the near future.

V. BIBLIOGRAPHY.

1.	Doebereiner	Annalen	(1832)	3	141
2.	Volhard	Annalen	(1891)	261	380
3.	Frankland & Aston	J C S	(1901)	79	515
4.	Curtius-Leimbach	J. Prakt.Chemie	(1833)	65,	23
5.	Schwanert	Annalen	(1860)	116	282
6.	Frankland	J C S	(1901)	79	516
7.	Lies	Annalen		100	327
8.	Freundler	French Bul.	(1897)	17	422

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